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Surface Chemistry of  $N_2H_4$  on Si(100)-2x1

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## Abstract

The adsorption and thermal decomposition of  $N_2H_4$  on  $Si(100)-2 \times 1$  were investigated using XPS, UPS, HREELS and LEED. Upon adsorption of 0.2 L  $N_2H_4$  on the surface at 100 K, partial dissociation of the NH bonds was indicated by the appearance of the Si-H stretching mode at 255 meV in HREELS and the 399.0 eV peak in  $N_{1s}$  XPS, which is assigned to the  $N_2H_x$  (presumably  $N_2H_3$ ) species. At lower dosages ( $D < 0.4$  L),  $N_2H_4$  adsorbed on  $Si(100)-2 \times 1$  in a side-on rather than an end-on geometry and hydrogen-bonding is likely to be formed in the overlayer adsorbates. The NN bond breaking process was observed to occur at 600 K; the  $NH_x$  products ( $x=0,1,2$ ) could be identified on the surface. At this temperature, the NN stretching mode essentially disappeared and the  $NH_2$  deformation and the NH stretching modes shifted from 200 and 413 to 192 and 420 meV, respectively. The same conclusion could also be established from the corresponding XPS and UPS results. Annealing the surface to higher temperatures caused further NH bond breaking, accompanied by the desorption of  $H_2$ , while N remained on the surface forming Si nitride.

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## 1. Introduction

The thermal nitridation of Si substrates has been studied extensively using different nitriding species, such as N [1,2], NO [3-6], NH<sub>3</sub> [7-17], HN<sub>3</sub> [18-19] and N<sub>2</sub>H<sub>4</sub> [20,21]. Among these different N-containing species, HN<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> molecules were employed more recently and they have been demonstrated to be very effective molecular nitriding agents for low-temperature organometallic chemical vapor deposition (OMCVD) processes on account of their high chemical reactivities [22-26].

In this study, we focus on the reactivity of the N<sub>2</sub>H<sub>4</sub> molecule on Si(100)-2x1 using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), high-resolution electron energy loss spectroscopy (HREELS) and low energy electron diffraction (LEED) techniques to monitor chemical changes occurring at the surface. Although there have been numerous investigations of N<sub>2</sub>H<sub>4</sub> reactions on metal surfaces in relation to the broad subject of NH<sub>3</sub>-metal surface chemistry, only a few studies have been reported on the reaction of N<sub>2</sub>H<sub>4</sub> on the single crystal surfaces of silicon [20,21], despite its relevancy to the Si<sub>3</sub>N<sub>4</sub> film deposition process.

The catalytic decomposition of N<sub>2</sub>H<sub>4</sub> on several metal surfaces has been investigated under ultra-high vacuum (UHV) conditions and the reaction mechanism was found to vary from surface to surface. For example, N<sub>2</sub>H<sub>4</sub> was found to molecularly adsorb on Ni(111) at 90 K and decompose at  $T_s > 285$  K to give NH<sub>3</sub>(g) and NH (a) species [27]. The annealing of the N<sub>2</sub>H<sub>4</sub>-dosed Fe(111) [28] and Al [29] surfaces, on the other hand, caused N<sub>2</sub>H<sub>4</sub> to dissociate into NH<sub>2</sub> (a), which further decomposed into N and H at higher temperatures. The NH<sub>2</sub> species was also produced on an Rh foil at lower N<sub>2</sub>H<sub>4</sub> dosages [30]. However, as the N<sub>2</sub>H<sub>4</sub> coverage was increased, other reaction channels, i.e., N-H bond breaking to give N<sub>2</sub>H<sub>x</sub> ( $x < 4$ ) species, occurred concurrently on the surface. In their XPS measurement, Truong et

al. [31] found that a partial dissociation of  $\text{N}_2\text{H}_4$  occurred on  $\text{Ru}(0001)$  at 200 K, presumably due to the NH bond break. Above 350 K,  $\text{N}_2\text{H}_x$  species further dissociated into  $\text{NH}_x$  species. The thermal decomposition of  $\text{N}_2\text{H}_4$  on  $\text{Pt}(111)$  was studied by Alberas et al. [32] using a variety of surface analysis techniques. The authors found that  $\text{N}_2\text{H}_4$  started to decompose through the breaking of NH bonds, not the NN bond, with the  $\text{N}_2$  product formed intramolecularly. The other gas phase product,  $\text{NH}_3$ , was produced by the hydrogenation of  $\text{N}_2\text{H}_4$ , i.e.,  $2\text{H}(\text{a}) + \text{N}_2\text{H}_4(\text{a}) \rightarrow 2\text{NH}_3(\text{g})$ .

We have recently reported the thermal decomposition of  $\text{N}_2\text{H}_4$  on  $\text{Si}(111)\text{-}7\times 7$  [20]. The  $\text{N}_2\text{H}_4$  decomposition process is similar to that of  $\text{N}_2\text{H}_4$  on  $\text{Ru}(0001)$  [31]; a partial dissociation of the NH bonds occurring upon the adsorption of  $\text{N}_2\text{H}_4$  on  $\text{Si}(111)$  at 120 K was verified by both XPS and more convincingly HREELS, in which the Si-H stretching mode could be clearly observed. However, appreciable NN bond breaking took place at temperatures above 600 K, which is much higher than that reported for  $\text{N}_2\text{H}_4$  on  $\text{Ru}(0001)$ .

The results of the present study on the interaction between  $\text{N}_2\text{H}_4$  and  $\text{Si}(100)\text{-}2\times 1$ , using HREELS, XPS, UPS and LEED techniques as mentioned above, will be compared with those for  $\text{N}_2\text{H}_4$  on  $\text{Si}(111)\text{-}7\times 7$ .

## 2. Experimental

The experiment was carried out in a custom-designed UHV system with a base pressure of  $< 1 \times 10^{-10}$  torr as reported elsewhere [20]. The  $\text{Si}(100)$  and  $\text{N}_2\text{H}_4$  samples were prepared in the same manner as described previously in ref. [20]. An Mg X-ray source was used for the XPS measurement and the electron energy analyzer was set at a pass energy of 50 eV, which gives an instrumental resolution of better than 1.3 eV (FWHM), a value observed for the  $\text{N}_{1s}$  XPS taken from a  $\text{Si}_3\text{N}_4$

sample. In our HREELS measurement, an electron beam with a primary energy of 5 eV was used. The typical elastic peak after scattering from a clean Si(100)-2x1 at 100 K has a counting rate of  $5 \times 10^5 \text{ s}^{-1}$  and an FWHM of 10 meV. The  $\text{N}_2\text{H}_4$  dosage was estimated according to ion gauge reading without calibration for the different gases.

### 3. Results and Discussion

#### 3.1 XPS

A series of  $\text{N}_{1\text{S}}$  XPS taken from a Si(100)-2x1 surface after exposing to the indicated amounts of  $\text{N}_2\text{H}_4$  dosage at 100 K are shown in Fig. 1. When 0.2 L  $\text{N}_2\text{H}_4$  was dosed on the surface,  $\text{N}_{1\text{S}}$  XPS spectrum presented a peak at 400.0 and a shoulder at 399.0 eV with an overall FWHM of 2.4 eV. Further dosing of  $\text{N}_2\text{H}_4$  shifted the 400 eV peak gradually to 400.9 at 4 L, while the 399 eV peak was suppressed. However, it was still visible as a lower energy tail. The higher energy peak originates from the molecularly adsorbed  $\text{N}_2\text{H}_4$  and its peak shift with increase of the  $\text{N}_2\text{H}_4$  is attributable to the condensing of the overlayer  $\text{N}_2\text{H}_4$  and the formation of hydrogen bonding between the adsorbates. Hydrogen bonding tends to stabilize  $\text{N}_{1\text{S}}$  electron in  $\text{N}_2\text{H}_4$ , and thus causes the peak shifting toward higher energies. Similar results were observed for  $\text{N}_2\text{H}_4$  on Fe(111) [28], Ru(0001) [31], Pt(111) [32] and Si(111)-7x7 [20]. When 5 L  $\text{N}_2\text{H}_4$  was dosed on Fe(111) at 126 K, a peak at 400.2 with an FWHM of 1.8 eV was found for the  $\text{N}_{1\text{S}}$  XPS. In this case,  $\text{N}_2\text{H}_4$  was believed to adsorb on the surface in a side-on geometry because an end-on adsorption would give rise to a much wider FWHM ( $\sim 3.5$  eV) due to the different chemical environment of the two N atoms in  $\text{N}_2\text{H}_4$  [28]. After flash-heating a 5 ML  $\text{N}_2\text{H}_4$  dosed Ru(0001) to 200 K, a peak at 399.0 eV was noted in addition to the 400.1 eV peak and the overall FWHM of the  $\text{N}_{1\text{S}}$  XPS was  $\sim 3.0$  eV. The 400.1 eV peak was attributed to the molecularly adsorbed  $\text{N}_2\text{H}_4$ , while a partial dissociation of the  $\text{N}_2\text{H}_4$  was suggested to be responsible for the

399.0 eV peak. Therefore, the observed large FWHM for the  $N_{1s}$  XPS at 200 K cannot be attributed to an end-on adsorption of  $N_2H_4$ . However, whether or not this 399.0 eV peak also existed at  $T_s=90$  K and at the submonolayer  $N_2H_4$  coverage was not reported. In the case of  $N_2H_4$  on Si(111)-7x7, the 399.0 eV peak could be observed at  $T_s = 120$  K and lower dosages ( $< 0.2$  L); it became more obvious after annealing a 0.4 L  $N_2H_4$  dosed sample to  $\sim 500$  K. The authors have attributed this peak more specifically to the  $N_2H_x$  ( $x=2,3$ ) species by analogy to the XPS results of  $NH_3$  on Si(111) and the assignment was supported by the observed Si-H stretching mode due to a partial breaking of NH bonds in the corresponding HREELS results.

Comparing these studies with the present one allows us to conclude that  $N_2H_4$  adsorbs on Si(100)-2x1 also in side-on geometry. The relatively large FWHM (2.4 eV) at 0.2 L dosage is ascribed to the coexistence of  $N_2H_x$  ( $x=2,3$ ) species, which exhibits the 399.0 eV peak. Other supporting evidence is the appearance of the Si-H stretching mode in the HREEL spectrum taken under essentially identical experimental conditions. Furthermore, as the  $N_2H_4$  dosage was increased, the overall FWHM of the  $N_{1s}$  XPS gradually decreased. This is because the relative contribution from the  $N_2H_x$  ( $x=2,3$ ) species became less important due to the lack of the active surface sites, and thus the spectrum was dominated by  $N_2H_4$  overlayers as indicated by the intensity increase and the B.E. shift of the 400 eV peak. At the highest dosage (4 L) employed in the present study, the thickness of the adsorbate is estimated to be  $\sim 10\text{\AA}$ , based on the corresponding  $Si_{2p}$  XPS signal attenuation measurements.

When the 4 L  $N_2H_4$  dosed Si(100) was warmed to 220 K, the 399.0 eV peak became more obvious (see Fig. 2) and the Si-H species also grew stronger as is evident in the corresponding HREELS results. At this temperature, the 399.0 eV peak overlapped with that of the 400 eV one to give a broad band centered at 399.6 eV. Clearly, these changes are caused by the further cracking of the NH bonds as

compared with the case of 0.2 L  $\text{N}_2\text{H}_4$  adsorbed on Si(100) at 100 K. On the other hand, the overall intensity attenuation of the  $\text{N}_{1\text{S}}$  XPS signal by 85% is due to the partial desorption of the adsorbates. As shown in Fig. 2, annealing the sample at 450 K caused the  $\text{N}_{1\text{S}}$  XPS peak shifting to 398.7 eV and its FWHM broadening to 2.8 eV with no obvious peak intensity change. These changes are attributable to the further breaking of the NH bonds and likely the NN bond in part of the adsorbate as well. The NN bond breaking essentially completed at 600 K, causing the  $\text{N}_{1\text{S}}$  peak to shift to 397.6 eV and its FWHM to reduce significantly. However, it is likely that the peak still has contributions from the higher energy components, the  $\text{NH}_x$  ( $x=1,2$ ) species [19]. Further annealing the sample at 800 and 1000 K completed the NH bond breaking as indicated by the narrowing and the shifting of the  $\text{N}_{1\text{S}}$  peak to 397.4 eV mainly due to the atomic N on the surface. Such a peak was reported earlier for  $\text{NH}_3$  [1,14] and  $\text{HN}_3$  [19] on Si after complete breaking of NH bonds. It was noted that the  $\text{N}_{1\text{S}}$  peak intensity increased slightly at 800 and 1000 K, especially the higher energy tails. This could be attributed to the readsorption of the N containing species desorbed from the sample holder during the sample annealing period. These species may be incompletely dissociated and thus give a higher energy tail in the  $\text{N}_{1\text{S}}$  XP spectrum.

It should be pointed out that X-ray irradiation can also induce the extraneous dissociation of adsorbates [7,20]. As a result, the XPS measurements may apparently show more dissociation of  $\text{N}_2\text{H}_4$  as compared with those observed in the corresponding UPS and HREELS results. This was obvious particularly at 600 K, where the 397.6 eV peak suggested a substantial breaking of the NH bonds. While in the UPS and HREELS measurements, as will be discussed later, the NH bond feature was still quite strong after the NN bond cracking at 600 K.

Before proceeding with a discussion of the UPS and HREELS results, we compare our XPS results with those of a TPD study for  $\text{N}_2\text{H}_4$  on Si(100) [21]. We

observed an  $N_{1s}$  XPS signal intensity decrease by 30% ( $I_{450K} = 70\% I_{220K}$ ), when the sample was annealed at 450 K. This  $N_{1s}$  signal intensity further decreased by another 10% at 600 K ( $I_{600K} = 90\% I_{450K}$ ). In their TPD measurements, Slaughter and Gland [21] found a broad  $N_2$  desorption peak at 400 K in addition to the 275 K peak and the peak near 460 K due to  $NH_3$  desorption. The observations from the two complementary techniques are consistent, although the  $N_{1s}$  XPS signal intensity decrease may also be caused by other effects, e.g., the geometry or the chemical environment of the N atom changes upon the annealing of the sample, such that the photoemission cross section for the  $N_{1s}$  electron is reduced. On the other hand, the fact that no obvious  $N_2$  and  $NH_3$  surface species could be detected in our surface analysis suggests that these species desorb from the substrate once they are formed. The adsorbed  $NH_3$  was not observed either in the studies of  $NH_3$  on Si(100) above 100 K [8, 14].

### 3.2 UPS

Fig. 3 shows the  $N_2H_4$  dosage effect on the Si(100)-2x1 surface states. As is evident in the figure, a peak at 0.8 eV below  $E_F$  is clearly seen in the He(I) UP spectrum taken from a clean surface at 100 K. This peak intensity gradually decreased with the increasing of  $N_2H_4$  dosage and vanished at  $\sim 0.4$  L. In a previous study of H on Si(100)-2x1, Himpsel et al. [33] observed a peak at 0.7 eV below  $E_F$  in He(I) UP spectrum, which disappeared as the surface was saturated with atomic H. Similarly, Hamers et al. [16] found a peak at 0.8 eV below  $E_F$  in their STM study of  $NH_3$  on Si(100). The authors attributed the 0.8 eV peak to the bonding "dangling bond" ( $\pi_b$ ) level, because the corresponding STM topograph from the occupied states showed rows of beam-shaped protrusions along the dimer rows with a maximum above the center of each dimer. They also observed another peak at 0.35 eV above  $E_F$  due to the anti-bonding level ( $\pi_a$ ). When the surface was exposed to  $NH_3$  at RT, the



elimination of the  $\pi_b$  surface states was evidenced by the observation that the 0.8 eV peak was replaced by a broad unstructured shoulder and by the appearance of a dip at 0.8 eV in the corresponding UP difference spectrum. Comparing the observed 0.8 eV peak intensity change with these results suggests that the surface states are also involved in the interaction between  $N_2H_4$  and the Si(100) surface, which caused the attenuation of the 0.8 eV peak in UPS. Furthermore, the elimination of the peak at 0.4 L  $N_2H_4$  dosage suggests a saturation or near-saturation of these Si "dangling bonds" which, in turn, suggested the formation of a complete layer of adsorption. Additional adsorption of  $N_2H_4$  would form overlayer adsorbates, which was indicated in the XPS results and can be seen from the He(II) UPS of  $N_2H_4$  on Si(100) as well.

The dosage and thermal effects on the He(II) UPS of  $N_2H_4$  on Si(100) are shown in Fig. 4. When 0.4 L  $N_2H_4$  was dosed on Si(100) at 100 K, two broad bands centered at 4.8 and 10.7 eV below  $E_F$  were observed. By analogy to the UPS results of  $N_2H_4$  in the gas phase [34,35] and adsorbed on Fe(111) at 126 K [28], these two bands can be assigned to the  $n^+$ ,  $n^-$  orbitals occupied by the lone electron pairs in the N atoms, the N-N and N-H orbitals, respectively. This was discussed in detail in ref. [20] for  $N_2H_4$  on Si(111)-7x7. The lower energy tail of the 10.7 eV peak is likely due to the presence of a small amount of  $N_2H_x$  ( $x=2,3$ ) species. Owing to the repulsive potential, the two lone electron pairs in the gaseous  $N_2H_4$  are rotated by  $\sim 90^\circ$  with each other, and thus they have slightly different energies. This difference could be further affected upon the adsorption of  $N_2H_4$  on the surface, because the  $N_2H_4$  molecule may change its configuration from a gauche form to an eclipsed form. However, such a subtle effect could be easily obscured by other effects, such as adsorbate-substrate and adsorbate-adsorbate interactions. Further dosing 1.6 L  $N_2H_4$  on the sample caused a shift of the 4.8 eV peak to 5.1 eV and a slight broadening of

the 10.7 eV peak, most likely due to hydrogen bonding between adsorbates. Similar observations were reported by Grunze in the study of  $\text{N}_2\text{H}_4$  on Fe(111) [28].

We noted that the lower energy tail of the 10.7 eV peak was suppressed by the further dosing of  $\text{N}_2\text{H}_4$ . Recalling the similar observation for the  $\text{N}_{1s}$  XPS peak at 399.0 eV, this lower energy tail could be related to the dissociatively adsorbed species,  $\text{N}_2\text{H}_x$  ( $x=2,3$ ). In fact, the gas-phase  $\text{N}_2\text{H}_2$  UPS showed peaks at 10.0, 14.4, 15.5 and 16.9 eV [36], while  $\text{N}_2\text{H}_4$  yielded peaks at 9.9, 10.6, 15.6 and 16.7 eV [34,35]. Therefore, a lower energy tail should be expected if the  $\text{N}_2\text{H}_x$  species were formed on the surface.

As the 2 L  $\text{N}_2\text{H}_4$  dosed sample was warmed to 220 K, the UP spectrum resembled that taken from the 0.4 L dosed sample at 100 K, except that the lower energy tail of the 10.7 eV peak became more obvious; indicating an increased contribution from the  $\text{N}_2\text{H}_x$  species. Annealing the surface at 450 K extended the tail down to 6 eV. In other words, the spectrum has now some contribution from the 7 eV peak because of the breaking of some NN bond and the formation of SiN bond. The 7 eV component became a distinct peak at 600 K, while the 10.7 eV peak intensity decreased. These changes indicate the cracking of the NN bond and the further breaking of the NH bond as well. Above 800 K, the UP spectrum is dominated by peaks at 4 and 7 eV with a tail at ~10 eV, which is very similar to that taken from an Si nitride sample prepared by annealing an NO dosed Si(100) at 1200 K to remove O atoms. Therefore, our 800 K UP spectrum indicates an essentially complete dissociation of the NH bonds and the formation of Si nitride.

### 3.3. HREELS

A series of HREELS taken from  $\text{N}_2\text{H}_4$  on Si(100)-2x1 at 100 K under different dosage conditions are shown in Fig. 5. When 0.2 L  $\text{N}_2\text{H}_4$  was dosed on the surface,

HREELS presented peaks at ~105, 138, 163 (shoulder), 200 and 413 meV due to NH<sub>2</sub> rocking, NN stretching, NH<sub>2</sub> wagging, NH<sub>2</sub> deformation and NH stretching vibrations, respectively. In addition, two humps at 60 and 70 meV could be probably attributed to the NH<sub>2</sub> torsional vibrations. These values match well with those of IR/Raman for solid N<sub>2</sub>H<sub>4</sub> [37] and also with the HREELS results of N<sub>2</sub>H<sub>4</sub> adsorbed on Pt(111) [32], Ni(111) [27] and Si(111)-7x7 [20]. Interestingly, a peak at 255 meV due to the Si-H stretching mode is clearly shown in the spectrum. This observation unambiguously indicates a partial cracking of the NH bonds upon the adsorption of N<sub>2</sub>H<sub>4</sub> on Si(100) at 100K. Further dosing N<sub>2</sub>H<sub>4</sub> caused no obvious peak shift, but the change of the relative peak intensities. The gradual decrease of the 255 meV peak due to the overlayer adsorbate suppression effect is indicative of the multilayer adsorption at increased N<sub>2</sub>H<sub>4</sub> dosages. Furthermore, the attenuation of the elastic peak (not shown here) and all other peaks (except that at 138 meV) seemed to suggest a disordered overlayer adsorption of N<sub>2</sub>H<sub>4</sub> on the surface. On the other hand, the increase of the relative intensity of the NN stretching mode at 138 meV is probably due to the fact that the first layer N<sub>2</sub>H<sub>4</sub> molecules adsorb on the surface in a side-on geometry while those in the overlayer have arbitrary orientations. In the HREEL spectrum of the 0.2 L N<sub>2</sub>H<sub>4</sub> dosed sample recorded at 12° off-specular angle (not shown here), the NN stretching mode was only a few times weaker than that recorded in the specular mode, while the corresponding elastic peak decreased by ~100 times in the off-specular spectrum. This off-specular angle HREELS measurement again supports a side-on adsorption of N<sub>2</sub>H<sub>4</sub> on Si(100) at 100 K with lower dosages established by the N<sub>1s</sub> XPS and the dosage-dependence HREELS results mentioned above.

The thermal effect on HREELS of a 0.6 L N<sub>2</sub>H<sub>4</sub> dosed Si(100) is summarized in Fig. 6. Upon warming this sample to 220 K, the HREEL spectrum is essentially the same as that taken from a 0.2 L N<sub>2</sub>H<sub>4</sub> dosed surface at 100 K. This observation

indicates a partial desorption of the adsorbates. However, by close examination of the spectrum we found that the relative intensity of the peaks at 200 ( $\delta_{\text{NH}_2}$ ) and 413 meV ( $\nu_{\text{NH}}$ , which is now shifted to 416 meV) decreased, while that of the Si-H stretching mode at 255 meV increased. These relative peak intensity changes suggest a further breaking of the NH bonds and the blue shift of the NH stretching mode is probably a reflection of the breaking of hydrogen bonding. At 450 K, the Si-H stretching mode grew further and the  $\text{NH}_2$  wagging mode at 162 meV became better resolved from the 138 meV peak, because of the continuing breaking of the NH bonds. On the other hand, the increase of the 105 meV peak suggests that some NN bond cracking also occurred concurrently at this temperature, since this peak is due mainly to the presence of  $\text{SiNH}_x$  ( $x=1,2$ ) species as reported in the studies of  $\text{NH}_x$  on Si surfaces [7-9,12,14].

After the sample was annealed to 600 K, the NN bond breaking virtually completed as indicated by the following observations: 1) The 105 meV peak became the dominant feature in the spectrum; 2) the 200 meV peak, due to the deformation mode of  $\text{NH}_2$  in  $\text{N}_2\text{H}_x$ , shifted to 192 meV, because the  $\text{NH}_2$  species fragmented on the surface; 3) the NH stretching mode shifted to 420 meV due to the  $\text{SiNH}_x$  ( $x=1,2$ ) species; 4) the 162 meV peak originated from the wagging mode of  $\text{NH}_2$  in  $\text{N}_2\text{H}_x$  disappeared. The remaining intensity at ~137 meV should have contributions from the bending vibration of the  $\text{Si}_2\text{NH}$  species in addition to the possibly survived NN containing species. The  $\text{Si}_2\text{NH}$  bending mode was reported at 144-6 meV in  $(\text{R}^1\text{R}^2\text{R}^3\text{Si})_2\text{NH}$  molecules [38], at 137 meV in the RI study of  $\text{NH}_3$  on a porous Si substrate [12] and in the HREELS for  $\text{NH}_3$  on  $\text{Si}(111)\text{-}7\times 7$  and  $\text{Si}(100)\text{-}2\times 1$  [14]. The fact that the 800-K HREEL spectrum is dominated by two peaks at 63 and 102 meV indicates an essentially complete dissociation of the NN and the NH bonds and the formation of Si nitride. The reappearance of the noticeable humps at ~160 and 200

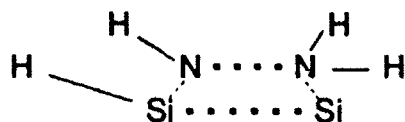
meV is likely due to the readsorption of the  $N_2H_x$  species as is also evident in the corresponding XPS results. Finally, the remaining SiH stretching mode was broadened and shifted to give a band centered at 267 meV, because some H atoms are now bonded to Si atoms which are back-bonded to N atoms.

#### 4. Discussion

The thermal decomposition of  $N_2H_4$  on Si(100) was investigated with XPS, UPS and HREELS. Partial dissociation of the NH bonds was found upon the adsorption of  $N_2H_4$  on the surface at 100 K, which continued upon the thermal treatment. Above 600 K, the NN bond breaking occurred on the surface. The decomposition process of  $N_2H_4$  on Si(100)-2x1 is essentially identical to that of  $N_2H_4$  on Si(111)-7x7. However, an interesting difference is noted; i.e., the 192 meV mode is much more intense for  $N_2H_4$  on Si(100) than on Si(111) after the NN cracking at 600 K. This result suggests that more  $NH_2$  species survived on Si(100) than Si(111) at this temperature, and thus supports the observation reported recently by Chen et al. [14] for  $NH_3$  on Si(100) and Si(111) surfaces. These authors found that  $NH_2$  is stable above 600 K on Si(100), but further dissociates into NH plus H on the Si(111) surface.

It was also noted that a peak at 65 meV appeared at 220 K, which became more intense at 450 K and then disappeared at 600 K. A peak at ~60 meV was observed in HREELS taken from Si nitride samples; e.g., peaks at 60 and 62 meV were reported by Taguchi et al. [5] and Edamoto et al. [2] for NO and N on Si(111) after annealing the sample to  $T_s > 1200$  K, respectively. In both cases, the peak was attributed to the formation of  $Si_3N_4$ . In the present study, however, the 65 meV peak appeared at very low surface temperature (< 600 K), at which no significant NN bond breaking occurred. Therefore, this peak cannot be due to the  $Si_3N_4$  species. The  $NH_2$  torsional vibration frequencies for  $N_2H_x$  may appear at ~65 meV, since they were observed at 50 and 81

meV in solid  $\text{N}_2\text{H}_4$ . Unfortunately, no such information is available for  $\text{N}_2\text{H}_4$  species to the best of our knowledge. On the other hand, we also speculate that the 65 meV peak may be related to the  $\text{N}_2\text{H}_3$  species adsorbed on the surface in a "ring" structure:



(see Fig. 7a), likely due to the Si-NN stretching and/or angle bending modes. For a Ti dinitrogen complex, (in which the two N atoms are bonded to two Ti atoms) an angle bending mode at 73 meV appeared in IR spectra [39].

The above structure is probably reasonable, because  $\text{N}_2\text{H}_4$  adsorbed on the surface in a side-on geometry as indicated in HREELS and XPS results and the Si dimers were involved in the bonding as indicated by the change of the 0.8 eV peak in He(I) UP spectra. In addition, the 65 meV peak was intense at 220 and 450 K, at which the  $\text{N}_2\text{H}_x$  concentration was higher. Furthermore, the disappearance of the peak at 600 K can be attributed to the breaking of the NN bond, and accordingly, the breaking of the "ring" structure (see Fig. 7c). It should be mentioned that, as the N-N distance in  $\text{N}_2\text{H}_4$  is only 1.45 Å [40], it is unlikely that  $\text{N}_2\text{H}_4$  adsorbs on Si(100)-2x1 across the two Si dimer rows because of the large distance between these dimer rows (~5.4 Å).

As to the partial NH bond dissociation at 100 K, it is not surprising because the NH bond strengths are about the same in both  $\text{N}_2\text{H}_4$  and  $\text{NH}_3$ , and  $\text{NH}_3$  was found to dissociatively adsorb on Si surfaces at 80 K. In addition,  $\text{N}_2\text{H}_4$  has a gauche form in gas phase, which may change upon the adsorption to allow both N lone electron pairs to interact with the surface. This could also enhance the dissociation of one of the NH bonds. At 450 K, the NH bond breaking occurred to a larger extent. However, we

believe that the dominant adsorbate is  $\text{N}_2\text{H}_3$  rather than  $\text{HNNH}$ , because after the NN bond dissociation at 600 K, the  $\text{NH}_2$  characteristic features are fairly strong in HEELS and there is no obvious  $\text{N}=\text{N}$  double bond formation at 450 K. The  $\text{N}=\text{N}$  containing species would give an  $\text{N}_{1s}$  XPS peak closer to that of the  $\text{N}_2$  feature (higher energy), but not the atomic N feature (lower energy) as observed by Alberas et al. in the case of  $\text{N}_2\text{H}_4$  on  $\text{Pt}(111)$  [32]. In the present study, no higher energy ( $\geq 400$  eV) components for  $\text{N}_{1s}$  XPS was observed at 450 K.

Above 600 K, the NN bond dissociation occurred on the surface. Intuitively, one would expect that the Si dimer bond should break concurrently. Since at 600 K LEED pattern preserved its  $2\times 1$  character, we proposed a structure as shown in Fig. 7c. According to this structure, the NH group forms bridge bonds with two Si atoms to give  $\text{Si}_2\text{NH}$  species and the  $\text{NH}_2$  species bonds to one of the unsaturated Si dangling bonds. The other Si dangling bond is occupied by the H species.

## 5. Conclusion

The adsorption and thermal decomposition of  $\text{N}_2\text{H}_4$  on  $\text{Si}(100)\text{-}2\times 1$  were investigated using XPS, UPS, LEED and HREELS. At 100 K,  $\text{N}_2\text{H}_4$  adsorbed on the surface in a side-on rather than an end-on geometry with a partial dissociation of the NH bonds as indicated by the presence of the SiH stretching mode in HREELS. The NH bond breaking continued as the sample was annealed at higher temperatures. Above 600 K, NN bond cracking occurred and the product  $\text{NH}_x$  ( $x=0,1,2$ ) species were identified on the surface. Interestingly, at this temperature, the  $\text{NH}_2$  characteristic features are stronger on  $\text{Si}(100)\text{-}2\times 1$  than  $\text{Si}(111)\text{-}7\times 7$ , suggesting that this species is more stable on the former surface. Further annealing the surface to  $T_s > 800$  K caused the complete dissociation of the NN and NH bonds and the desorption of the H-species, while atomic N remained on the surface to form Si nitride.

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### Figure Captions:

Fig. 1 The  $N_{1s}$  XPS taken from  $N_2H_4$  on Si(100)-2x1 at 100 K and at the indicated dosages.

Fig. 2 The thermal effect on the  $N_{1s}$  XPS of the 4 L  $N_2H_4$  dosed Si(100). All spectra were taken by annealing the sample at the indicated temperatures for 100 sec. and then cooling down to 100 K for 5 min.

Fig. 3 He(I) UP spectra showing the  $N_2H_4$  dosage effect on the surface states of the Si(100)-2x1 surface at 100 K. The peak at 0.8 eV below  $E_F$  gradually decreased with the increase of the  $N_2H_4$  dosage and disappeared at 0.4 L dosage.

Fig. 4 The thermal effect on the He(II) UP spectra of the 2.0 L  $N_2H_4$  dosed Si(100). All spectra were recorded after annealing the sample at the indicated temperatures for 100 sec and cooling to 100 K for 5 min. The bottom curve was obtained after dosing 0.4 L  $N_2H_4$  on Si(100) at 100 K.

Fig. 5 The HREELS taken from  $N_2H_4$  on Si(100) at 100 K and at the indicated  $N_2H_4$  dosages.

Fig. 6 The thermal effect on the HREELS of the 0.6 L  $N_2H_4$  dosed Si(100). All spectra were recorded after annealing the sample at the indicated temperatures for 100 sec. and then cooling down to 100 K for 5 min.

Fig. 7 The proposed model for the adsorption geometry of  $N_2H_4$  on Si(100)-2x1 at different temperatures.

Fig. 1

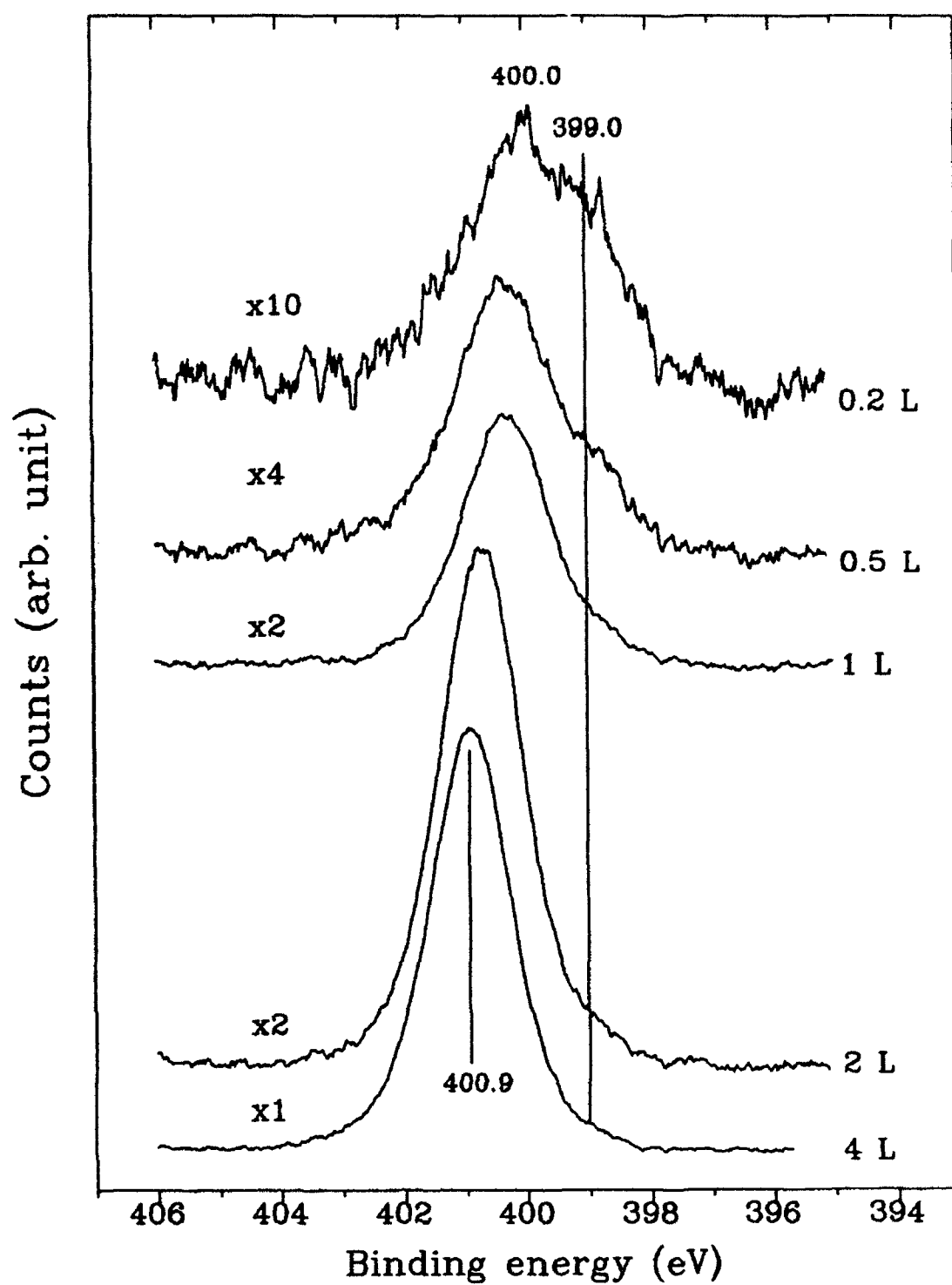


Fig. 2

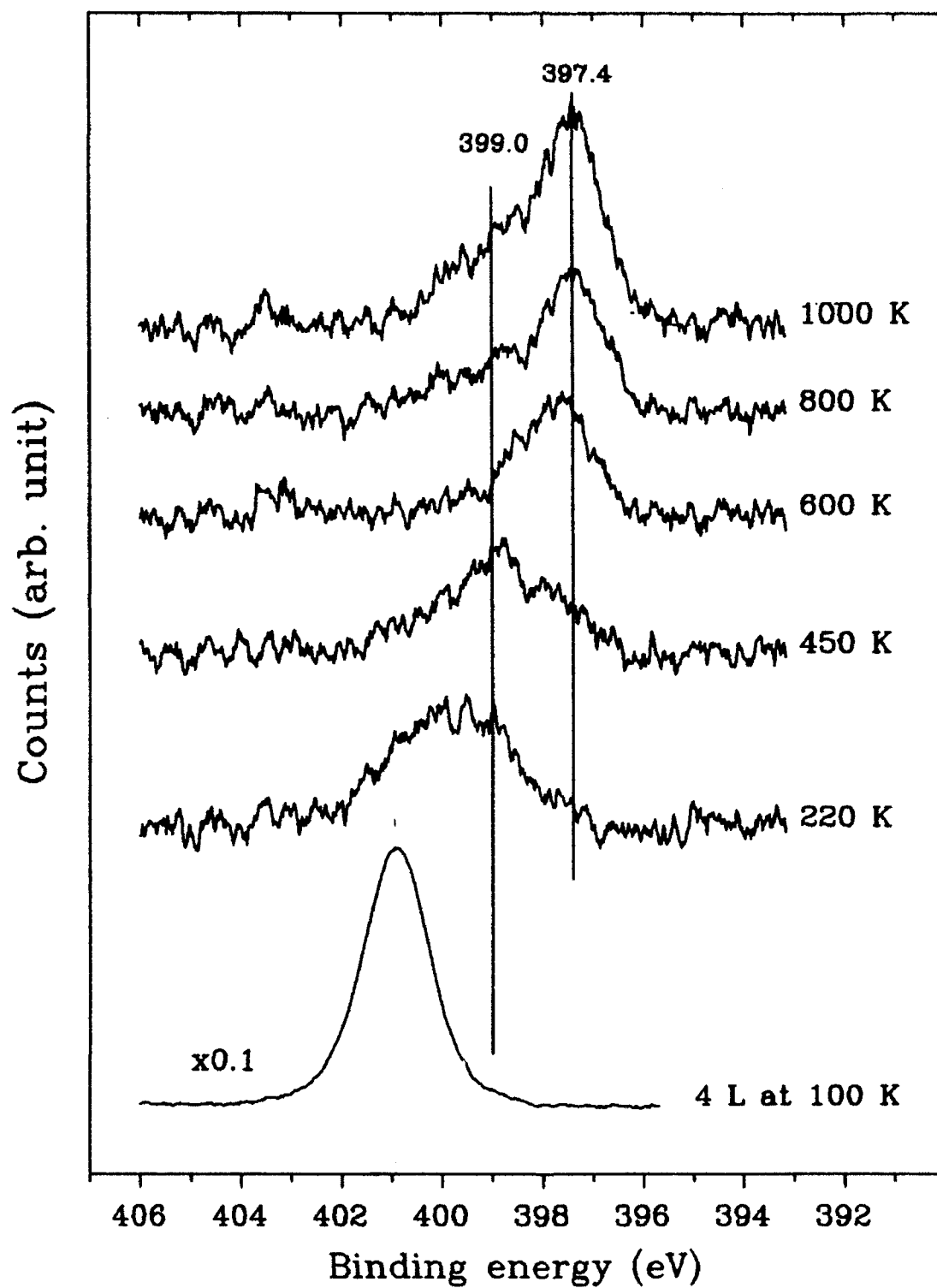


Fig. 3

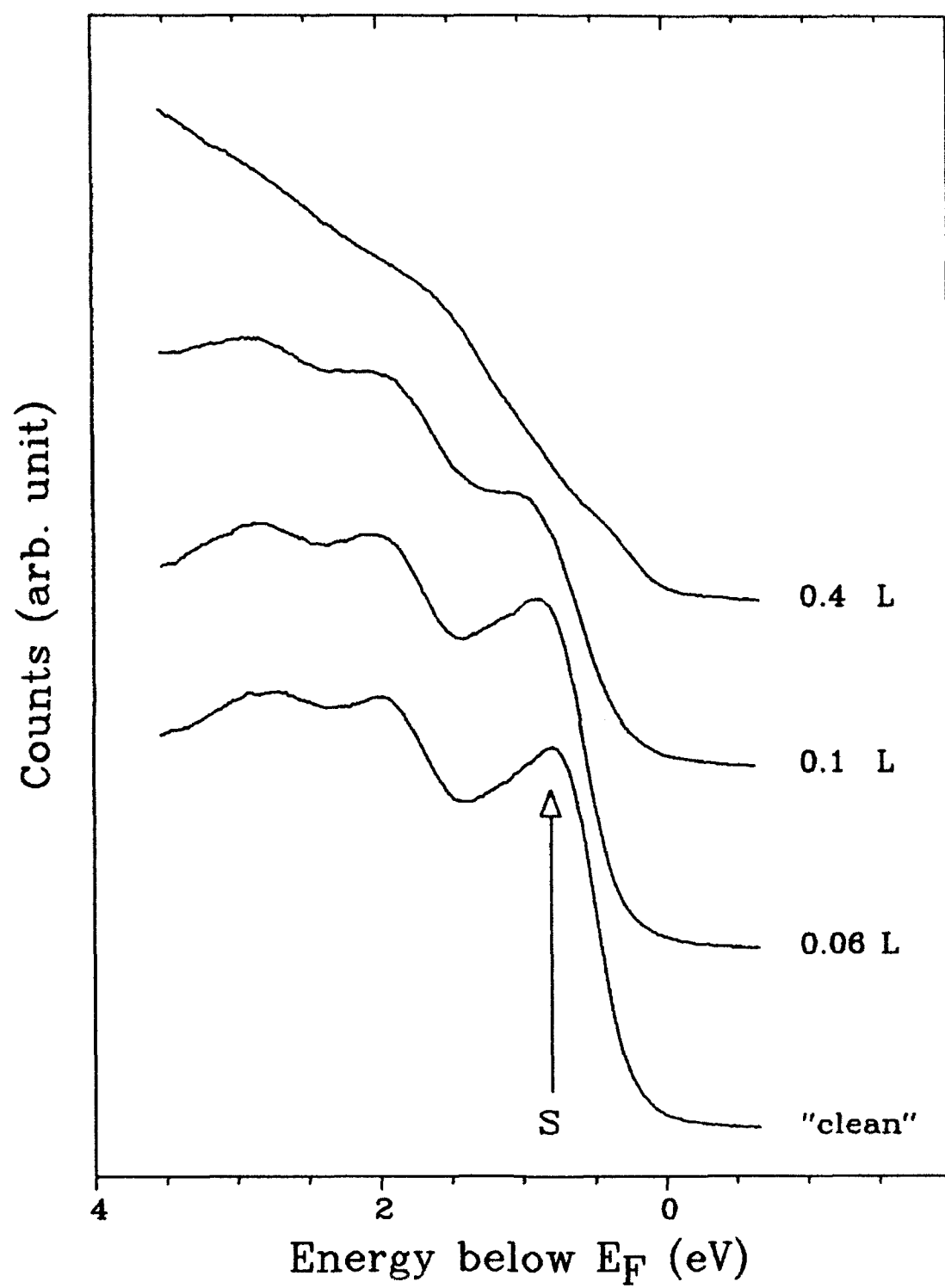


Fig. 4

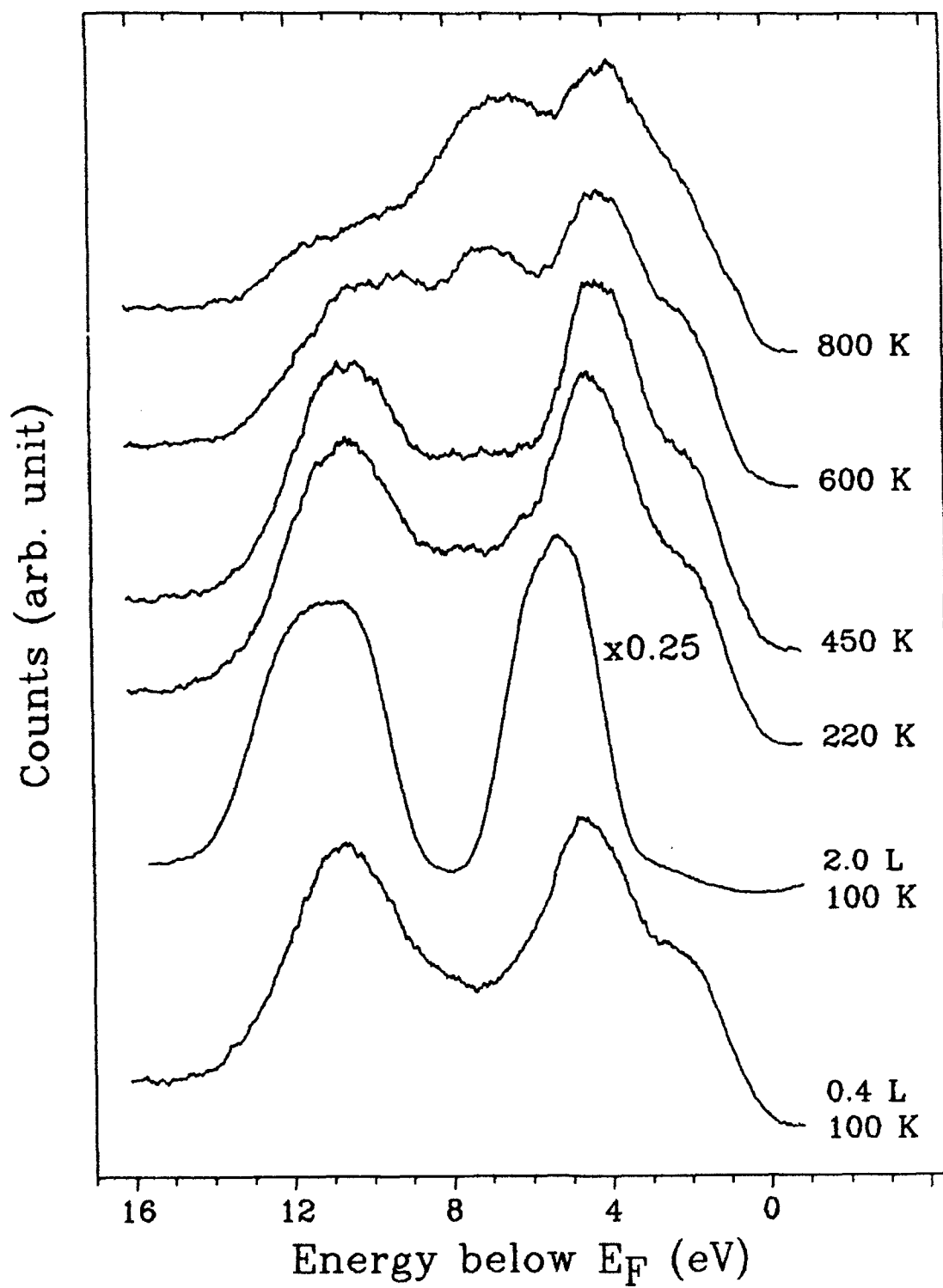


Fig. 5

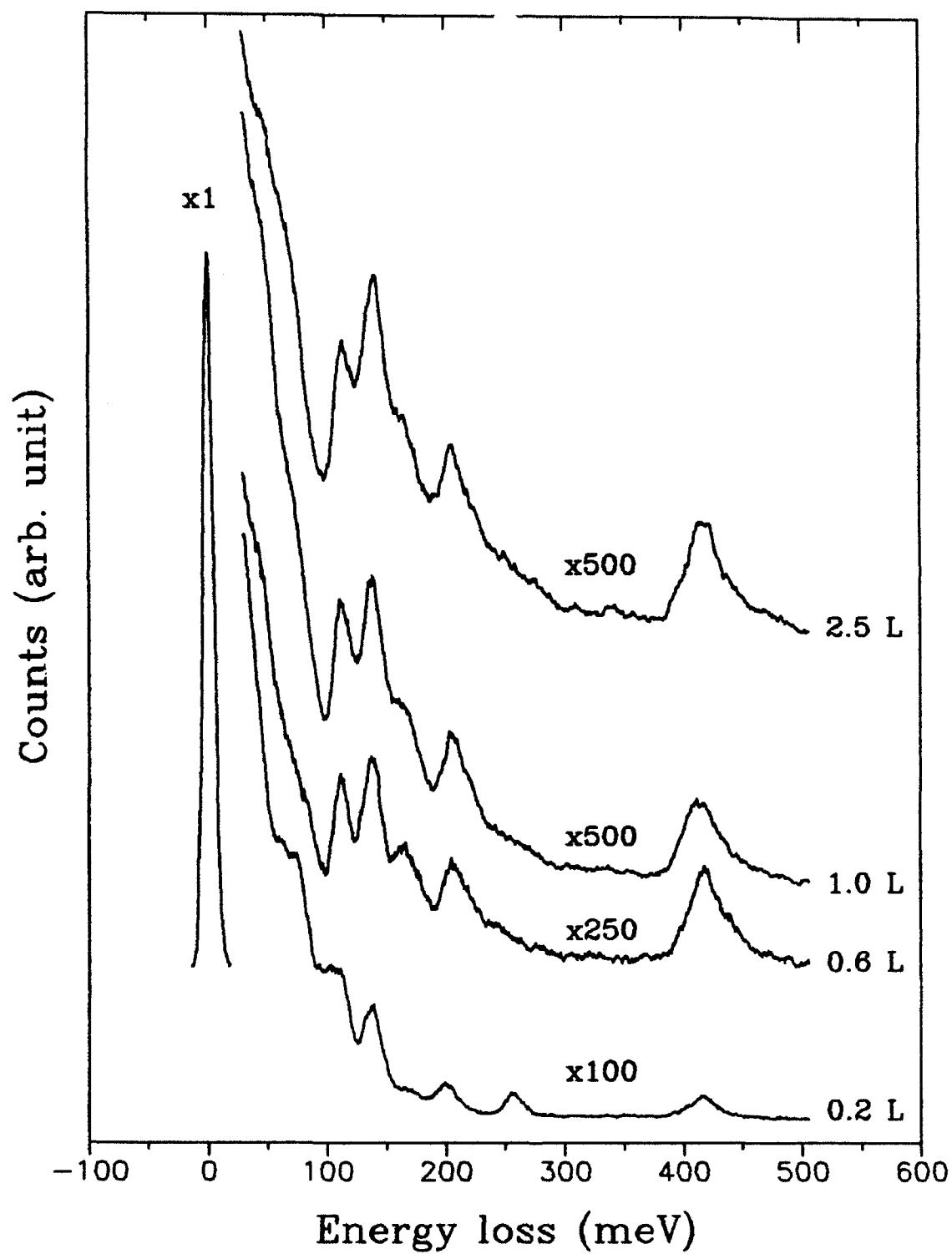


Fig. 6

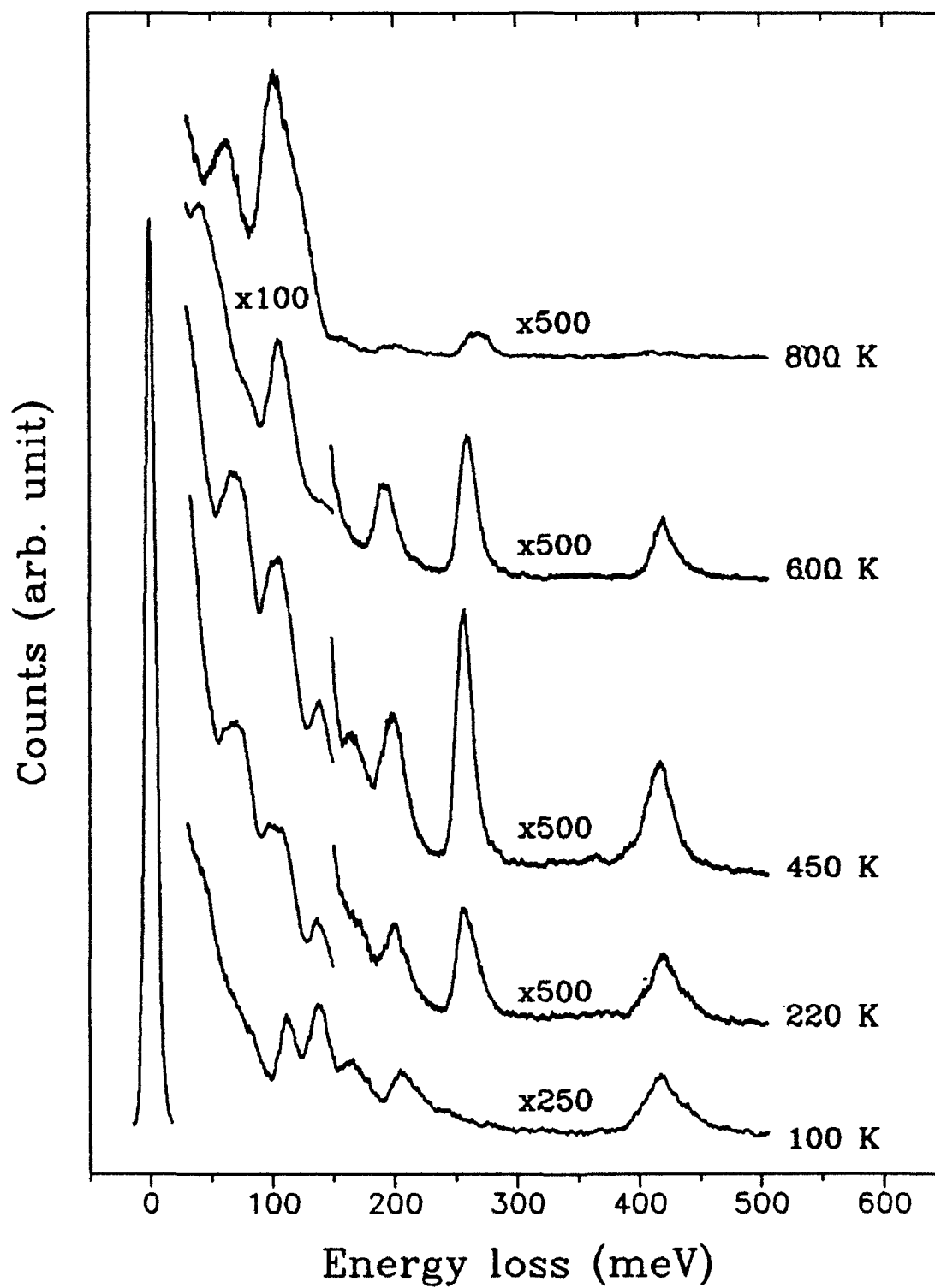




Fig. 7

